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SECONDARY BATTERY

[Niji Denchi]

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Specification

1. Title of the invention

Secondary battery

2. Patent Claims

1. A secondary battery characterized by the facts that it consists of an anode, an electrolytic solution, and a cathode and that its cathodic material includes a compound of an alkali metal or alkaline earth metal and carbon.

2. A secondary battery specified in Claim 1 characterized by the fact that the addition ratio of the compound of an alkali metal or alkaline earth metal and carbon within the aforementioned cathodic material is 0.1 ~ 10 wt%.

3. A secondary battery specified in Claim 1 or 2 characterized by the fact that, in a case where the aforementioned alkali metal, alkaline earth metal, and carbon are defined as A, B, and C, respectively, the x value and y value of compounds expressed by C_xA and C_yB are $1 \sim 36$ and $1.5 \sim 2$, respectively.

4. A secondary battery specified in Claim 1, 2, or 3 characterized by the fact that the aforementioned compound of an alkali metal or alkaline earth metal and carbon is Li_7C_7 , Na_7C_7 , K_7C_7 , Cs_7C_7 , C_7Li , C_7Li , $C_{17}Li$, $C_{27}Li$, $C_{37}Li$, C_7Na , $C_{17}Na$, $C_{27}Na$, C_4K , $C_{14}K$, $C_{32}K$, CaC_2 , Mg_2C_3 , or their mixture.

¹ Numbers in the margin indicate pagination in the foreign text.

5. A secondary battery specified in Claim 1, 2, 3, or 4 characterized by the fact that the aforementioned cathodic material is bound by an elastomer such as polyethylene, polypropylene, ethylene rubber, ethylene-propylene rubber, butylene rubber, polyvinylidene fluoride, etc.

6. A secondary battery specified in Claim 1, 2, 3, 4, or 5 characterized by the fact that the anodic material of the battery that uses the aforementioned cathodic material is a metal oxide which contains at least one type of metal selected from among manganese, chromium, cobalt, vanadium, and molybdenum.

3. Detailed explanation of the invention

(i): Industrial application fields

The present invention concerns a secondary battery constituted by a cathode which includes an alkali metal or alkaline earth metal (e.g., lithium, etc.) as an active material and an anode which includes a metal oxide (e.g., manganese dioxide, etc.) as an active material.

/2

(ii): Prior art

This type of secondary battery is problematic in that the lithium included as a cathodic active material entails an internal short-circuit and a shortened recharge & discharge cycle life as a result of its branched growth on the cathode surface during a recharge phase and of its subsequent encroachment into the anode.

A cathode constituted by a lithium alloy has been proposed as a measure against this problem. Most importantly, in a case where lithium is used alone and where the lithium becomes eluted, in the form of an ion, as a result of a discharge, a depression & protrusion pattern becomes formed on the cathode surface, and during subsequent recharge operations, the lithium becomes electrodeposited on the protrusion in a concentrated manner and then grows in a branched fashion, whereas in a case where a lithium alloy is used, lithium becomes regenerated during a recharge phase in such a way that it will form an alloy with the metal that constitutes a substrate, which is advantageous in that the branched growth of the lithium can be inhibited.

The lithium alloys which have been used in the prior art, however, are brittle, and furthermore, it is difficult to bind them by using binders, due to which the formation of a fine powder and/or electrode desorption may occur during recharge & discharge cycles, which is problematic in that the cycle performances deteriorate.

In the context of providing cathodic materials endowed with excellent cycle performances, furthermore, the use of a graphite interlayer compound wherein lithium, which becomes doped and/or dedoped in the course of recharge & discharge cycles, is internalized within a crystal (Japanese Patent Publication Kokoku No. Sho 60[1985]-23433), the use of an n-doped form of a carbonaceous material which satisfies certain crystal thickness and true density requirements (Japanese Patent Application

Publication Kokai No. Sho 62[1987]-90863), the use of a material wherein lithium is stored within a carbonaceous material (e.g., coke, etc.), etc. have been proposed.

(c): Problems to be solved by the invention

In a case where lithium is stored within a carbonaceous material according to these proposals, however, a conspicuous spontaneous discharge becomes incurred during preservation, and furthermore, the capacitance becomes depleted as a result of the repetition of recharge & discharge cycles, which represents a new shortcoming.

(d): Mechanism for solving the problems

The present invention, which has been conceived in acknowledgment of these problems, is characterized by the use of a compound of an alkali metal or alkaline earth metal and carbon such as lithium carbide (Li_2C_2), calcium carbide (CaC_2), etc. as a cathodic material.

(e): Functions

It becomes possible, according to the present invention, to obtain a secondary battery accompanied not only by a minimal spontaneous discharge but also by a minimal discharge capacitance loss even in a case where recharge & discharge cycles are repeated.

(f): Application examples

Figure 1 is a diagram which shows a lengthwise cross-sectional view of the secondary battery of the present invention, whereas (1) in the same figure is a cathode which consists of a lithium alloy and which represents the marrow of the present invention, and it is adhered, under pressure, to the cathodic collector (3), which is attached fixed to the inner bottom plane of the cathodic can (2). (4) is an anode which has been obtained by mixing, with magnesium oxide, which served as an active material, an acetylene black electroconductivizing agent and a fluorinated resin binder at a ratio (weight ratio) of 80 : 10 : 10 by molding the obtained mixture, and by then contacting, under pressure, the molded product with the inner bottom plane of the anodic can (5).

(6) is a separator made of a polypropylene non-woven fabric, whereas this separator is impregnated with a non-aqueous electrolytic solution obtained by solubilizing 1 mole/L of lithium perchlorate into a volume equivalent solvent mixture of propylene carbonate (PC) and 1,2-dimethoxyethane (DME). (7) is an insulating packing which electrically insulates the anodic and anodic cans. Dimensionally speaking, the battery diameter and thickness are 25 mmφ and 3.0 mm, respectively.

Next, examples for preparing the cathode (1), in which the essence of the present invention lies, will be discussed in detail.

Preparation Example 1

Lithium and carbon were mixed with one another at a molar ratio of 1 : 1, and after the obtained mixture had then been reacted at 1,200°C within dry argon, it was cooled and pulverized, as a result of which an Li_2C_2 powder was prepared. The Li_2C_2 powder thus prepared was mixed with a coal-type pitch coke, and after this mixture had been mixed with an ethylene rubber, which served as a binder, at a ratio of 90 : 10 (volume ratio), the obtained mixture was compressively molded at a pressure of 1.5 t/cm², as a result of which an electrode with a diameter of 20 mm and a thickness of 1.0 mm was obtained. This electrode was electrolyzed within $\text{LiClO}_4\text{-PC} + \text{DME}$ until the potential of the carbonaceous material in relation to lithium had reached 0 V, as a result of which lithium became stored within the carbonaceous material, and the cathode (1) was obtained. A secondary battery of the present invention was prepared by using this cathode (1).

In this context, the addition ratio of Li_2C_2 within the cathode (1) is critical from the standpoint of the battery performances, and as Table I and Figure 2 indicate, in a case where the
/3
addition ratio of Li_2C_2 is 0.1 wt% (battery A1) or below, the residual capacitance after a 1-month preservation period at room temperature drops below 90%, whereas in a case where the addition ratio of Li_2C_2 exceeds 10 wt% (battery A5), the cycle life deteriorates quickly. It is therefore desirable for the addition ratio of Li_2C_2 within the cathode (1) of the present invention to

be confined to a range of 0.1 ~ 10 wt% [(battery A1) ~ (battery A5)]. Batteries 1, 2, and 3 are shown for comparative purposes. Incidentally, the test conditions were designated as follows in this case: A discharge was induced at a discharge current of 3 mA until the achievement of 2 V, whereas a recharge was induced at 3 mA until the eventual achievement of 3.5 V.

Table I

Battery	1	2	A1	A2	A3	A4	A5	3
Addition ratio of Li_2C_2 (wt%)	0	0.05	1.0	0.5	1.0	5.0	10	15

Preparation Example 2

A battery was prepared according to procedures identical to those in Preparation Example 1 except that Na_2C_2 was used in place of Li_2C_2 and that polyvinylidene fluoride was used as a binder. Its performances are shown in Table II and Figure 3. Batteries B1 ~ B5 are batteries of the present invention, whereas batteries 4, 5, and 6 represent comparative examples. It can be seen that in this battery of Preparation Example 2, too, it is desirable for

the addition ratio of Na_2C_2 within the cathode (1) to be confined to a range of 0.1 ~ 10 wt%.

Table II

Battery	1	2	B1	B2	B3	B4	B5	3
Addition ratio of Na_2C_2 (wt%)	0	0.05	1.0	0.5	1.0	5.0	10	15

Incidentally, in addition to Li_2C_2 and Na_2C_2 instantiated respectively in Preparation Examples 1 and 2, others can also be used as compounds to be added to the cathode (1) so long as they are compounds of alkali metal carbon [sic: Presumably "alkali metals"] and carbon such as K_2C_2 , Cs_2C_2 , C_7Li , C_7Li , C_{14}Li , $\text{C}_{??}\text{Li}$, $\text{C}_{??}\text{Li}$, C_7Na , C_{14}Na , $\text{C}_{??}\text{Na}$, C_7K , C_{14}K , and C_{32}K and/or compounds of alkaline earth metals and carbon such as $\text{CaC}_?$, Mg_2C_3 , etc., and it is also possible to use their mixtures.

In other words, it can be seen that the x value of a compound expressed by CxA in a case where the alkali metal and carbon are defined respectively as A and C is confined to a range of 1 ~ 36 and that the y value of a compound expressed by CyB in a case

where the alkaline earth metal and carbon are defined respectively as B and C is confined to a range of 1.5 ~ 2.

As binders for binding cathodic materials other than the ethylene rubber and polyvinylidene fluoride, furthermore, it is also possible to use polyethylene, polypropylene, ethylene-propylene rubber, and/or butylene rubber.

As active materials of the anode (4) of the battery other than manganese, furthermore, it is also possible to use metal oxides which include at least one type selected from among chromium, cobalt, vanadium, and molybdenum such as molybdenum trioxide, vanadium pentaoxide, cobalt oxide, etc.

As has been mentioned earlier, it becomes possible, according to the present invention, to obtain, by using, as a cathodic material, a carbonaceous material which includes a compound of an alkali metal or alkaline earth metal and carbon (e.g., Li_2C_2 , CaC_2 , etc.), a secondary battery accompanied not only by a minimal spontaneous discharge but also by a minimal discharge capacitance loss even in a case where recharge & discharge cycles are repeated.

The present inventors postulate the following reasons for this phenomenon.

Carbonaceous materials are generally characterized by crystalline structures wherein carbon atoms are coupled mainly in hexagonal configurations, whereas the hexagonal structure cannot be perpetuated at coupling terminals, due to which carbon atoms present at such terminal sites become easily coupled with the

oxygen and/or water contents of air, resulting in the formation of a hydroxyl group (COH) and/or carbonyl group (COOH). These functional groups become reacted, due to their high activities, with electrolytic solutions, as a result of which the electrolytic solutions may become decomposed, or the lithium stored within the carbonaceous material may become reacted with these functional groups during recharge phases, thus serving as factors contributing to spontaneous discharges. It is therefore necessary to lower the activities of these functional groups in advance, and this method is used in the present invention. In other words, in a case where a compound of an alkali metal or alkaline earth metal and carbon represented by Li_2C_2 is added to a carbonaceous material, such a compound becomes reacted with the hydroxyl group or carbonyl

/4

group within the carbonaceous material, as a result of which these functional groups become transformed, and it becomes possible to prevent the reaction of the lithium being stored within said carbonaceous material with the aforementioned functional group and therefore to inhibit the spontaneous discharge. Unlike lithium alloys, furthermore, these carbonaceous materials are not brittle, and since they can be easily bound by using a binder such as an elastomer, etc., it presumably becomes possible to inhibit the fine powderization of the electrode despite repeated storages and releases of lithium in the course of recharge & discharge cycles and accordingly to prepare a battery endowed with excellent cycle performances.

(g): Effects of the invention

As the foregoing explanations have clearly demonstrated, the cathodic material of the present invention includes a compound of an alkali metal or alkaline earth metal and carbon represented by Li_2C_2 , Na_2C_2 , etc., and it becomes possible to form a secondary battery endowed with excellent cycle performances and accompanied by a minimal spontaneous discharge, due to which its industrial value is extremely high.

Although flat batteries were instantiated in the aforementioned application examples, it goes without saying that similar effects are achieved in the cases of cylindrical batteries as well.

4. Brief explanation of the figures

Figure 1 is a diagram which shows a lengthwise cross-sectional view of the battery of the present invention, whereas Figures 2 and 3 are respectively performance diagrams which show the cycle performances and preservation performances of the batteries of the present invention and batteries of comparative examples.

(1): Cathode; (4): Anode.

Applicant: Sanyo Electric Corp.

Agent: Takushi Nishino, patent attorney, and two others

Figure 1

第1図

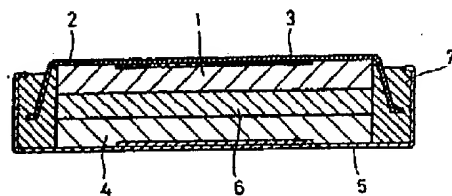
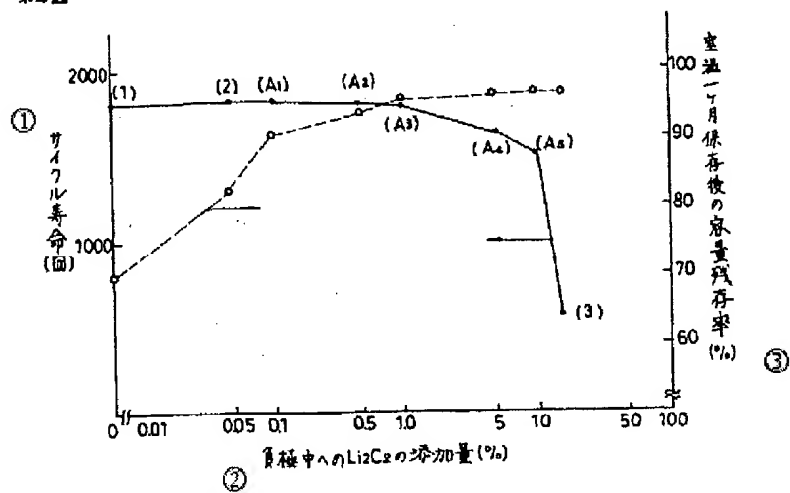


Figure 2

第2図

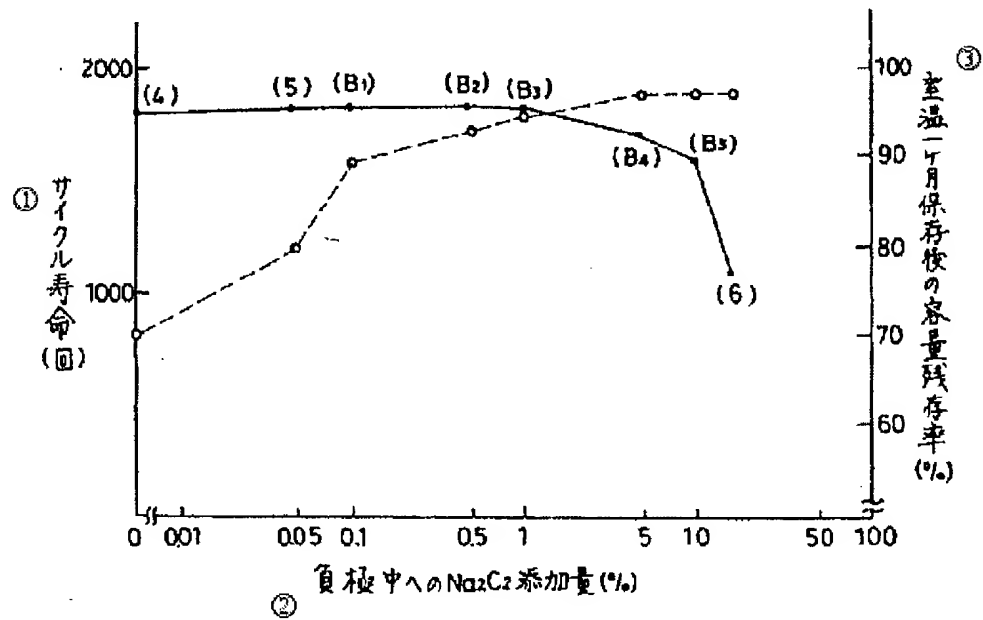


[(1): Cycle life (N); (2): Addition ratio of Li_2C_2 within the cathode (%); (3): Residual capacitance after a 1-month preservation period at room temperature (%)]

Figure 3

/5

第3図



[(1): Cycle life (N); (2): Addition ratio of Na_2C_2 within the cathode (%); (3): Residual capacitance after a 1-month preservation period at room temperature (%)]

Procedural Amendment Report (spontaneously issued)

December 18, Hei 2[1990]

Dear Chief Judge of the Patent Agency:

[Stamped, "Pass"]

1. Display of the case

Japanese Patent Application Tokugan No. Hei 2[1990]-252355

2. Title of the invention

Secondary battery

3. Amending party

Relation to the case: Patent applicant

Name: (188) Sanyo Electric Corp.

4. Agent

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[Stamped, "Patent Agency, December 20, Hei 2[1990]"]

5. Objects of amendments

(1): "Detailed explanation of the invention" section of the specification

6. Contents of amendments

(1): "Table II" on page 8 of the specification is amended as follows:

Re

Table II

Battery	4	5	B1	B2	B3	B4	B5	6
Addition ratio of Na_2C_2 (wt%)	0	0.05	1.0	0.5	1.0	5.0	10	15